Catalytic combustion of volatile organic compounds in binary mixtures over MnOx/Al$_2$O$_3$ catalyst

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A B S T R A C T

In this work the catalytic performance of an alumina supported manganese oxide catalyst in ethanol, ethyl acetate, toluene and mixtures of them was studied. The reactivity of each VOC investigated increased in the following order: ethanol > ethyl acetate > toluene. Toluene affects acetaldehyde yields, favoring partial combustion of ethanol and ethyl acetate. There is a competition for the adsorption sites between ethanol and ethyl acetate because both are polar molecules. Mixture effect decreases when the conversion temperature range of each component in the mixture is different, as in the case of ethanol–toluene and ethyl acetate–toluene mixture, consequently, the total conversion temperature is determined by the temperature at which the most difficult molecule is oxidized, in this case toluene.

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1. Introduction

Volatile organic compounds (VOCs) are considered as great contributors to the atmospheric pollution [1,2] and dangerous for their effect on the human health [3]. Catalytic combustion is one of the most interesting technologies, from the economical point of view, for the destruction of emissions of VOCs, compared to the incineration process. In fact, catalytic oxidation occurs at lower temperatures with higher yields of destructions than thermal oxidation.

Many catalysts used in total oxidation reactions are based on noble metals (platinum, palladium, rhodium) usually supported on metal oxides granular pellets such as Al$_2$O$_3$, TiO$_2$, ZrO$_2$, or on ceramic or metallic monoliths. However, transition metal oxides (mainly Co, Cu, Ni and Mn [4]) have also demonstrated a very good catalytic performance in oxidation reactions. Moreover they have lower costs and higher resistance to poisons [5].

Industrial exhaust gases usually present mixtures of volatile organic compounds of different chemical character such as aromatic hydrocarbons, alkanes, oxy-derivatives (alcohols, acetates and ketones). Studies of the catalytic activity on a single molecule of VOC partially represent the catalyst application. Therefore, it should be of interest to test the catalytic activity not only in the reaction of one organic compound oxidation in the air stream, but also in the oxidation of multi-component mixtures. It has been reported that the oxidation of a VOC in a mixture differs from its single oxidation due to the interactions of the different species with the catalyst. The mixture effect is very difficult to predict a priori, usually an inhibiting effect [6–9], and very rarely promoting effect was observed when two-component mixtures were oxidized. [10] Besides the possible inhibiting or promoting effects, changes have been observed in the selectivity to by-products when mixtures of VOCs are oxidized [8].

The aim of this work is to study the catalytic behaviour of a catalyst based on a manganese oxide supported on alumina in the combustion of VOCs generally found in emissions of the printing industries, ethanol, toluene and ethyl acetate. The catalytic performance in the oxidation of the VOCs separately or in two-component mixtures was evaluated.

2. Experimental

2.1. Catalyst description

The details of the synthesis method have been reported in a previous paper [11]. Briefly, the alumina support (θ-δ-Al$_2$O$_3$ with a specific surface area of 102.5 m^2/g) was impregnated until incipient wetness with a Mn(NO$_3$)$_2$·4H$_2$O (Merk) solution in multiple stages with drying in between at 100 °C for 1 h. Finally, the sample was dried at 70 °C overnight and calcined at 500 °C for 3 h. The deposited manganese oxide (11.25 wt% of Mn) was identified as MnO$_2$ by means of X-ray diffraction (XRD). However, the results of temperature programmed reduction (TPR) showed

that the oxidation state was 3.2 indicating the existence of amorphous Mn_2O_3 species since they are not detected by XRD.

2.2. Catalytic evaluation

A glass reactor of fixed bed at atmospheric pressure was used. Data were obtained in steady state. A sample of 300 mg (0.5–0.8 mm particle diameter) diluted with glass particles of the same size in a ratio 1:5 was used. The composition of the feed was 0.5% and 1% in volume in the case of the oxidation of single VOCs at a total flow rate of 100 ml/min. The oxidation of two-component mixtures was followed using a 1:1 molar ratio and keeping the feed composition at 1% in volume of total VOCs. The reagents and reaction products were analyzed on line using two chromatographs with thermal conductivity detector: a Buck 910 equipped with a Carbowax 20M/Cromosorb W column in which the VOCs were analyzed, and a Shimatzu 8A with a Carbosphere column to detect CO, CO_2 and O_2.

The conversion of VOC, X(%), was defined as:

$$X\% = \frac{VOC_{in} - VOC_{out}}{VOC_{in}} \times 100$$

where $[VOC]_{in}$ means VOC (ethanol, ethyl acetate or toluene) inlet molar concentration and $[VOC]_{out}$, the VOC outlet molar concentration.

The following abbreviations were used to indicate the VOC composition in the feed: ethanol 0.5% = E0.5; ethanol 1% = E1.0; ethyl acetate 0.5% = A0.5; ethyl acetate 1% = A1.0; toluene 0.5% = T0.5; toluene 1% = T1.0.

2.3. Temperature programmed surface reaction (TPSR)

The TPSR of single and mixtures of VOCs on the catalyst were carried out in ultrahigh vacuum (1.1×10^{-5} Pa) using a mass quadrupole spectrometer Balzers (QMG 112 A). The samples previously treated at 100 °C in He flow were saturated with several pulses (0.5 μl) of a single VOC or a VOC mixture. The desorption experiments were performed with a He flow of 45 ml/min increasing the temperature from 100 °C to 450 °C at a heating rate of 10 °C/min.

3. Results and discussion

3.1. Catalytic performance in single VOCs combustion

The catalytic performance of this catalyst in single VOCs combustion is shown in Fig. 1. The catalytic reactivity of the oxidized compounds decreased in the following order: ethanol > ethyl acetate > toluene. It can be observed that the conversion of each VOC decreases as the composition of the VOC in the feed increased, this is expected since the contact time is shorter. Particularly, the slope of the ethanol conversion curve changes with the feed composition. Higher conversions in the range of high temperatures are reached, decreasing the difference between E0.5 and E0.1 conversion curves. This fact may be due to the adiabatic increase of the temperature in the catalyst surface, which is produced as a consequence of the reaction heat. The reactor thermocouple is located on the head of the catalytic bed, though the measured temperature corresponds to an average value and it does not exactly correspond to the real temperature of the surface of the catalyst where the reaction proceeds. This temperature could be determined if the reaction velocity were known. Thus, the maximum temperature increase (ΔT_{max}) could be calculated, but this study is beyond the aim of the present work. Evidently, the increase in the catalyst surface temperature is higher when a higher composition of ethanol is fed.
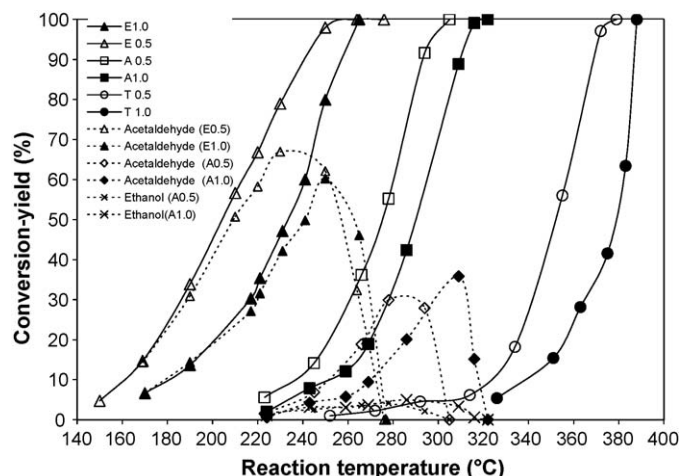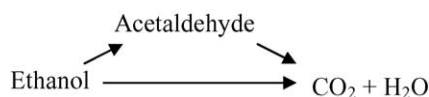

Fig. 1. VOCs conversion and product yields vs. reaction temperature.

In the process of ethanol oxidation, apart from the products of total combustion (CO_2 and H_2O), a product of incomplete oxidation, acetaldehyde, was detected. The oxidation of ethanol may run according to the following scheme:

Ethanol → Acetaldehyde → CO_2 + H_2O

When ethyl acetate was oxidized, ethanol and acetaldehyde were found in the flue gas. Probably in a first stage ethyl acetate partially hydrolyzes to acetic acid and ethanol, and this last one finally oxidizes through acetaldehyde to CO_2 and H_2O. The acetic acid would not be stable and it would decompose quickly. In general the scheme of these reactions can be represented as follows:

Ethyl acetate → Ethanol → Acetaldehyde → CO_2 + H_2O
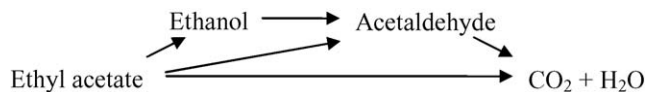
Acetaldehyde is a volatile organic compound more noxious for human health than ethanol, therefore it is interesting to analyze the acetaldehyde yield as a function of the reaction temperature (Fig. 1). Higher values of acetaldehyde yield were obtained during ethanol oxidation, with maximum values around 60–65%, while during ethyl acetate oxidation the maximum acetaldehyde yield reached 35%. In this case it is also observed a maximum ethanol yield lower than 10%. During toluene oxidation no intermediates were detected, only total combustion products, CO_2 and H_2O were detected. The close of the carbon balances indicate that no other undetected product is formed during the reaction.

Pure alumina was also evaluated in order to analyze the influence of the support on the catalyst activity. No combustion products were detected. Only small amounts of dehydration products were detected at 220 °C when ethanol combustion was evaluated. It is important to notice that this product was not detected during ethanol combustion on the manganese oxide catalyst.

3.2. Catalytic performance in VOCs binary mixtures

In order to study the potential application of this catalyst for the treatment of actual industrial emissions, the catalytic performance was evaluated in the combustion of three binary mixtures: ethyl acetate–ethanol (A + E), ethyl acetate–toluene (A + T) and ethanol–toluene (E + T).
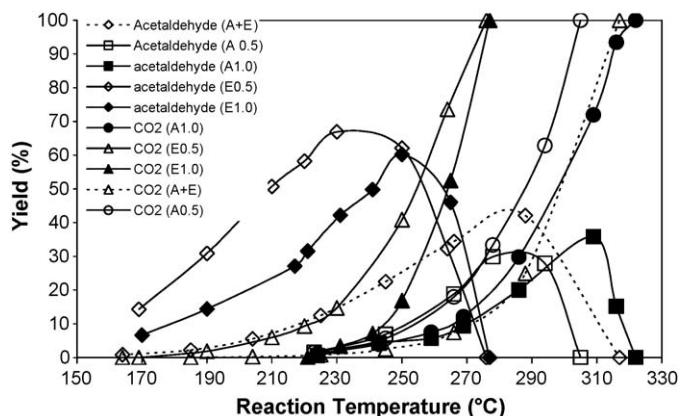
Fig. 2. Product yield vs. reaction temperature during E, A and A + E combustion.

3.2.1. Ethyl acetate–ethanol mixture

The influence between the components of a binary mixture will be more important when the oxidation reactions of both molecules take place in the same temperature range. Hence, it is interesting to study the ethyl acetate–ethanol mixture combustion.

The effect of the ethyl acetate presence on ethanol combustion cannot be analyzed from conversion vs. reaction temperature data, since ethanol is also a by-product of the ethyl acetate combustion. Therefore, the mixture effect will be analyzed from the acetaldehyde and CO_2 yield results, Fig. 2. The acetaldehyde maximum yield produced during ethanol combustion is higher than the one produced during ethyl acetate combustion. However, the temperatures at which acetaldehyde is completely converted are higher in the case of ethyl acetate. The acetaldehyde and CO_2 yields obtained during the mixture combustion are lower than the ones produced during pure ethanol combustion, which would demonstrate that the presence of ethyl acetate inhibits ethanol combustion.

Considering ethyl acetate combustion, it can be observed that the CO_2 yield obtained during the mixture combustion is lower than the one obtained during A0.5 oxidation, however, the CO_2 yield vs. temperature curve is similar to that obtained during A1.0 oxidation. Thus, ethyl acetate combustion is affected by the presence of another molecule, in this case ethanol, or by the presence of the same molecule as it occurs during A1.0 oxidation.

It is known that the adsorption of VOCs on the surface of the catalyst is governed by the polarity of the molecule. In this case both molecules are polar thus a competition for the adsorption sites could exist, and this competition would be reflected in the catalytic combustion. In order to study if the adsorption capacity of the VOCs on the catalyst surface could affect their reactivity, TPSR measures of single compounds and mixtures of them were made. During ethyl acetate desorption only $m/z = 44$ (CO_2), $m/z = 18$ (H_2O) and $m/z = 31$ (ethanol) signals were detected. The signal corresponding to ethyl acetate, $m/z = 43$, was not detected. Pure ethanol desorbs at low temperatures (~193 °C), which indicates a weak adsorption, and at higher temperatures (>300 °C) it desorbs as CO_2 and H_2O, reacting on catalyst surface. Fig. 3 shows the TPRS profiles of pure ethanol and ethyl acetate and the mixture of them, following $m/z = 31$ signal (ethanol). Ethanol desorbs at lower temperatures in presence of ethyl acetate indicating a weaker adsorption. The ethanol produced during ethyl acetate adsorption desorbs at lower temperature than ethanol in mixture, which would indicate that ethyl acetate is more strongly adsorbed than ethanol. Evidently there is a competition for the adsorption sites because both molecules are polar, which explains the inhibiting effect on ethanol combustion.
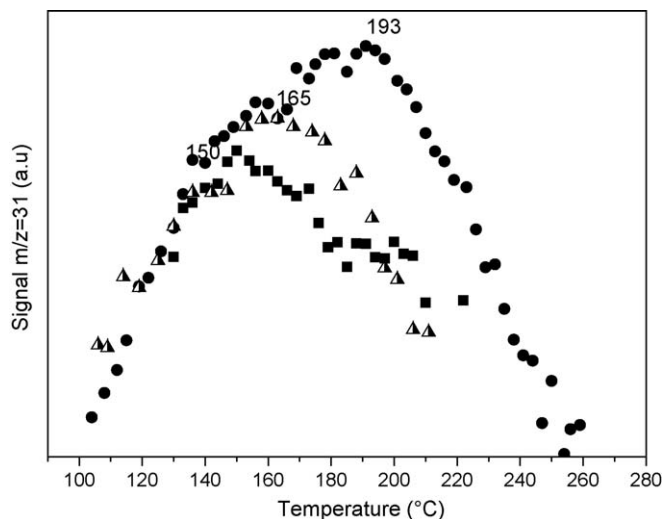

Fig. 3. TPSR of pure ethanol (●), ethyl acetate (■) and ethanol–ethyl acetate mixture (▲). Following $m/z = 31$ (ethanol).

3.2.2. Ethyl acetate–toluene mixture

Ignition curve, VOC conversion vs. temperature, is the most widespread way of catalytic activity evaluation in deep oxidation studies. These curves are frequently characterized by two parameters, T_{50} and T_{80}, which correspond to the temperatures needed to reach 50% and 80% conversion, respectively. Table 1 shows the values of these parameters in the combustion of A0.5, A1.0, T0.5, T1.0 and A + T. The presence of toluene produces a promoting effect on the ethyl acetate combustion. This molecule is activated at lower reaction temperatures. The higher conversion of ethyl acetate is translated in a higher acetaldehyde production in comparison to the combustion of A0.5, see Fig. 4. It is also observed that the presence of toluene does not affect the production of ethanol, but lower CO_2 yield in the whole range of reaction temperatures is obtained. This fact may indicate that toluene favors the partial combustion of ethyl acetate to acetaldehyde. Similar results were reported by Musialik-Piotrowska et al. [12] in the simultaneous combustion of toluene and selected oxy-derivative compounds over supported perovskite catalysts. They found that toluene strongly inhibited the oxy-derivatives oxidation and increased the concentration of yielded by-products.
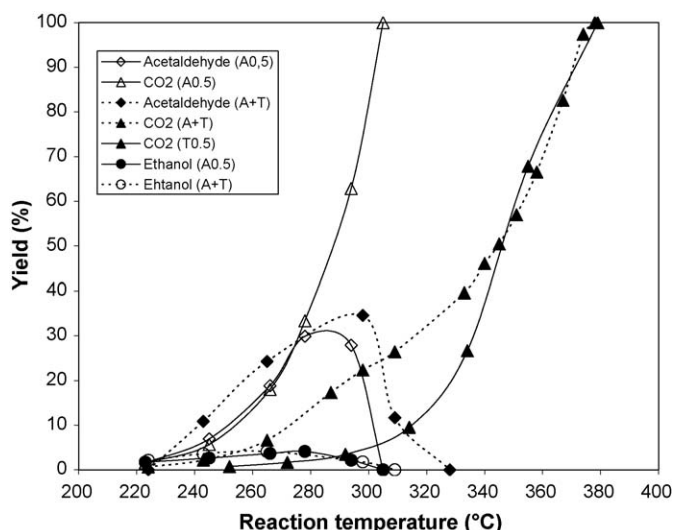

Fig. 4. Product yield vs. reaction temperature during A, T and A + T combustion.

Table 1
Catalytic activity.

	Toluene conversion			Ethyl acetate conversion			Ethanol conversion		
	COV	T_{50}	T_{80}	COV	T_{50}	T_{80}	COV	T_{50}	T_{80}
	T0.5	345	360	A0.5	275	288	E0.5	205	232
	T1.0	379	386	A1.0	290	305	E1.0	234	250
	A + T	358	370	A + T	270	285	A + E	245	280
	E + T	355	370	A + E	286	305	E + T	213	240

Ethyl acetate is completely oxidized before toluene conversion starts. Thus, it would be expected that toluene conversion were not affected by ethyl acetate presence. However, toluene oxidation is inhibited by the presence of ethyl acetate and this inhibition could be due to the effect of the higher concentration of total VOC in the feed. However, when the conversion of toluene in mixture is compared to the conversion of T1.0, the inhibition should be higher. Another inhibitory effect could be the presence of CO_2 and H_2O, products of total combustion of ethyl acetate, since they are the only products present in the mixture at the temperature range of toluene combustion. In order to study this effect, the combustion of toluene was evaluated in the presence of CO_2 and H_2O (Fig. 5). These products were fed in the same proportion as they are produced during ethyl acetate combustion. Toluene is strongly inhibited by the presence of CO_2 and H_2O. Auer et al. [13] also explain the inhibition in methane combustion by the presence of CO_2 and H_2O formed during ethylene combustion. It has been published [14] that the adsorption of water on the active sites decreases the catalyst activity. Thus, the decrease in catalytic activity can be explained by a competition of VOCs and water for specific sites. However, in this case, toluene conversion in mixture was higher than toluene conversion in CO_2 and H_2O presence. These results let us think that an additional effect would compensate the inhibition of toluene oxidation. This effect could be an increase of catalyst surface local temperature due to the exothermical character of the ethyl acetate oxidation.

In general when more than one component is oxidized simultaneously, a competition for the adsorption sites between the molecules might exist. The component which is adsorbed preferentially is oxidized first. In this case ethyl acetate is a more polar molecule than toluene so it would be expected that ethyl acetate adsorbs more strongly on the catalyst surface than toluene. As it was previously established, ethyl acetate is strongly adsorbed on the surface giving the reaction products, ethanol, CO_2 and H_2O. During toluene desorption $m/z = 44$ and $m/z = 18$ signals were detected and the signal $m/z = 91$ corresponding to toluene was not
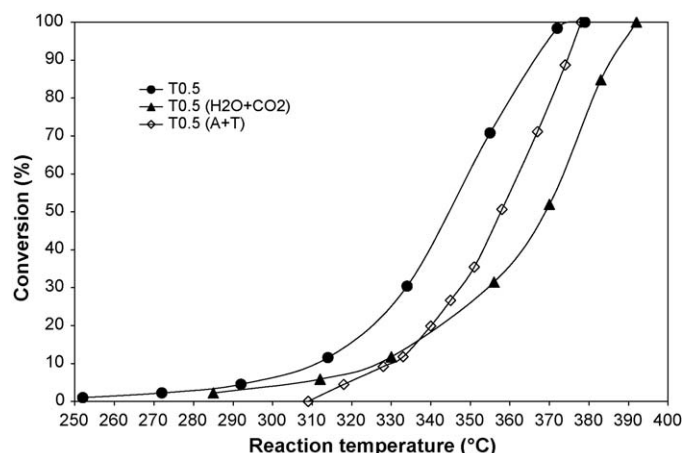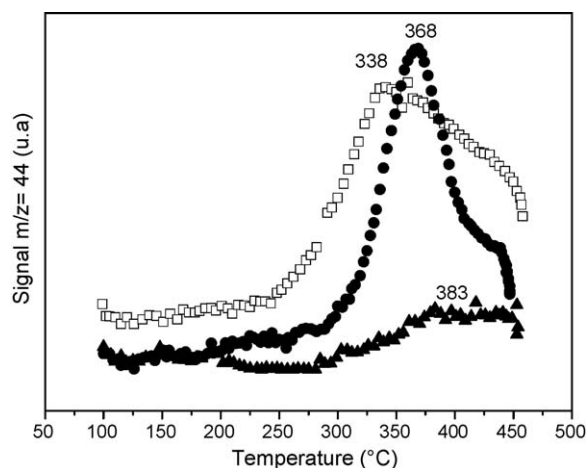
Fig. 6. TPSR of pure toluene (▲), ethyl acetate (●) and ethyl acetate–toluene mixture (□). Following $m/z = 44$ (CO_2).

detected. This could indicate that the molecules are strongly adsorbed and react at the catalyst surface giving the reaction products, or that the adsorption of the molecules is poor giving small amounts of CO_2 and H_2O. In Fig. 6, the CO_2 signals obtained by the desorption of pure toluene and ethyl acetate are presented. As it can be seen a lower CO_2 amount is detected during the toluene desorption. This would indicate that there is a poor adsorption of toluene on the catalyst surface, whereas a higher adsorption of ethyl acetate exists on the surface – as it was expected–, since more polar molecules are preferentially adsorbed. Following the CO_2 evolution in the mixture desorption, it is observed that CO_2 desorption maximum shifts to lower temperatures when toluene is fed together with ethyl acetate, compared to the CO_2 desorption curve from pure ethyl acetate indicating a weaker adsorption on the surface. Even though ethyl acetate is more strongly adsorbed on the surface than toluene, toluene modifies the ethyl acetate combustion increasing the acetaldehyde selectivity. This fact could indicate that the oxidation of ethyl acetate and toluene occur through different reaction mechanisms. With the aim to analyze if this mixture effect is also observed in another mixtures composed by an aromatic and an oxy-derivative components, the ethanol–toluene mixture was studied.

3.2.3. Ethanol–toluene mixture

Another interesting effluent to study is the ethanol–toluene mixture since alcohols and aromatics are in the extremes of reactivity in oxidation reactions. It can be observed, see Table 1, that the presence of toluene slightly inhibits ethanol conversion, reaching the 50% of conversion at higher temperatures (10 °C) than the corresponding to the oxidation of the single compound. Moreover, toluene increases the by-product (acetaldehyde) yield, Fig. 7. Higher values of maximum yield and higher reaction temperatures are obtained, reaching total oxidation of acetaldehyde 35 °C above the temperature at which it is single oxidized. It is also observed a lower CO_2 yield when the mixture is oxidized in the temperature range of ethanol conversion. This fact would indicate that the effect of toluene on the ethanol combustion is the same one than on the combustion in the ethyl acetate–toluene mixture, favoring the partial oxidation of ethanol to acetaldehyde.

Toluene conversion is also inhibited by ethanol presence but to a lesser extent by the presence of ethyl acetate. It is well known that mixture effect decreases when the conversion temperature range of each component in the mixture is different, consequently, the total conversion temperature will be determined by the temperature at which the most difficult molecule is oxidized, in this case toluene.
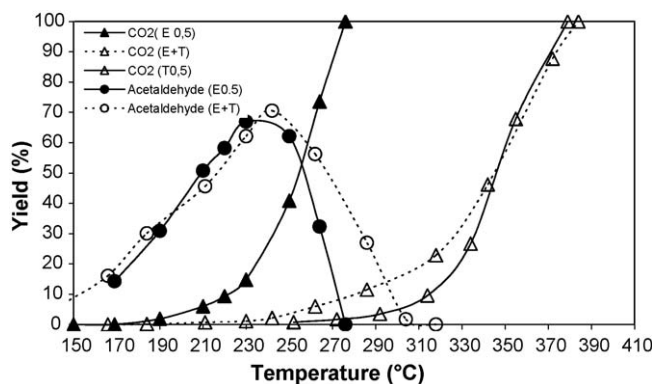
Fig. 5. Toluene conversion vs. temperature reaction.

Fig. 7. Product yield vs. reaction temperature during E, T and E + T combustion.

Ethanol is preferentially adsorbed on the surface because it is a more polar molecule than toluene, thus, it is more easily oxidized. From TPSR curves of pure ethanol and in mixture with toluene, Fig. 8, it can be observed than in toluene presence the ethanol curve shifts to lower temperatures indicating a weaker adsorption on the surface. Although toluene is poorly adsorbed, as it was concluded during the discussion of the ethyl acetate–toluene mixture, it affects ethanol adsorption, explaining in this way the lower ethanol conversion observed.

Consequently, it could be suggested that the first stage of ethanol oxidation process is the adsorption of the molecule on the surface and then it reacts with the lattice oxygen of the catalyst through a Mars-van Krevelen mechanism [15]. Further, the TPSR measures have been made in absence of oxygen and despite this, reaction products have been detected, revealing the catalytic role of the oxygen species of the catalyst [16]. The poor adsorption of toluene on the catalyst surface even in absence of ethanol, could indicate that the oxidation of toluene does not occur from chemisorbed species on the surface, but it would mainly react with chemisorbed oxygen species on the catalyst surface, following a Rideal-Eley mechanism. This was also suggested by Burgos et al. [17], on Pt catalysts supported over anodized aluminum monoliths. Costa et al. [18], have proposed that the acetaldehyde formed during partial oxidation of ethanol on Pd/CeO_2 catalysts could desorb and then react with the chemisorbed oxygen on the surface to give CO_2 (g). Thus the delay in the oxidation of acetaldehyde produced during ethanol combustion should be due to a competition with toluene for the chemisorbed

oxygen atoms on the catalyst. Even if ethanol is more strongly adsorbed on the surface than toluene, it is toluene which reacts easily with the chemisorbed oxygen on the catalyst. In other words, there is no competition for the adsorption sites between toluene and ethanol, but the main competition exists for the chemisorbed oxygen atoms on the catalyst. This would corroborate the above proposed for the ethyl acetate–toluene mixture combustion.

4. Conclusions

The reactivity of each VOC investigated increased in the following order: ethanol > ethyl acetate > toluene. The combustion products were CO_2 and H_2O in the case of toluene combustion, acetaldehyde, CO_2 and H_2O in the case of ethanol combustion and acetaldehyde, ethanol, CO_2 and H_2O in the case of ethyl acetate combustion. The higher amount of acetaldehyde was detected during ethanol combustion.

During the combustion of ethyl acetate–ethanol mixture, there is a competition for the adsorption sites because both are polar molecules. That explains the inhibiting effect of ethyl acetate on ethanol combustion since ethanol adsorbs more weakly on the surface than ethyl acetate.

Toluene affects acetaldehyde yields, favoring partial combustion of ethanol and ethyl acetate. Even if more polar molecules (ethanol and ethyl acetate) are more strongly adsorbed on the surface than toluene, it is toluene which reacts easily with the chemisorbed oxygen on the catalyst. In other words, there is no competition for the adsorption sites, but the main competition exists for the chemisorbed oxygen atoms on the catalyst.

Mixture effect decreases when the conversion temperature range of each component in the mixture is different, as in the case of ethanol–toluene and ethyl acetate–toluene mixtures; consequently, the total conversion temperature is determined by the temperature at which the most difficult molecule is oxidized, in this case toluene. Thus it is concluded that Al_2O_3 supported manganese oxide catalyst is appropriated to treat effluents containing mixtures of VOCs since the mixture conversion temperatures are practically similar to that of the component which is most hardly oxidized.

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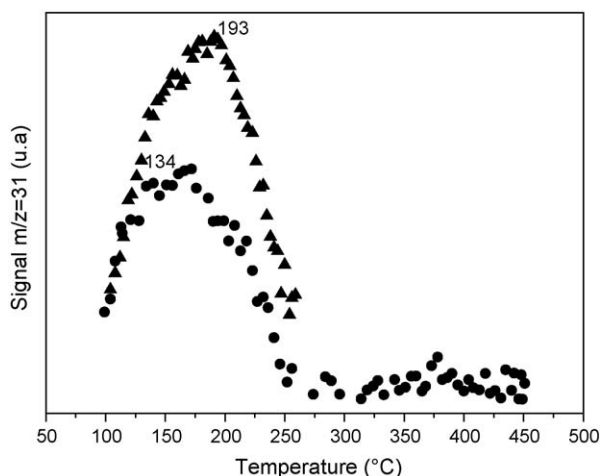**Fig. 8.** TPSR of pure ethanol (▲) and ethanol–toluene mixture (●). Following $m/z = 31$ (ethanol).